

Advanced Transmission Electron Microscopy of Pu Alloys

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Introduction

The characterization of microstructural changes in Pu-Ga alloys resulting from storage and aging phenomena is an important technical challenge to the nuclear Stockpile Stewardship program. We have identified at least two age-related phenomena that may occur in Pu alloys, dimensional changes due to the initial transient, helium accumulation, and void swelling, and phase instability. The initial transient is a well-known effect that results from the initial cascade damage. This form of dimensional change tends to saturate within approximately two years. A second contributor to dimensional change is the build-up of helium as a result of the alpha decay. Helium is generated at a rate of approximately 40 parts per million per year. Positron annihilation results by Howell¹ indicate that the helium atoms will quickly fill a nearby vacancy and diffuse through the lattice as a helium filled vacancy. Void swelling is potentially the most severe mechanism of dimensional change in Pu alloys. It has been observed in all materials exposed to irradiation, but has yet to be seen in naturally aged Pu.

Phase instability is a potential concern due to the fact that the δ -phase is thermodynamically metastable at room temperature. Timofeeva² has shown that the δ -phase will decompose to δ -phase and Pu_3Ga given enough time at ambient temperature. At sub-ambient temperatures, the δ -phase undergoes a displacive or martensitic phase transformation to the monoclinic α' -phase, which is approximately 20% more dense. Phase transformations such as these would result in density changes, dimensional changes, and changes in mechanical properties.

Traditional characterization techniques such as optical microscopy, x-ray diffraction and scanning electron microscopy are insensitive to many of the age-related microstructural changes. In this investigation, we have applied advanced transmission electron microscopy (TEM) to investigate the microstructure and bonding of Pu alloys. A 300 keV Phillips CM300FEG with a field emission gun electron source and Gatan Imaging Filter are used for the investigations.

Results

Advanced TEM has been used to characterize the helium bubble distribution in new and old Pu alloys. Figure 1a shows a TEM micrograph of He bubbles in a 42-year old material. These results have been coupled to rate equation modeling to predict the evolution of He bubble number density and average size with size as shown in Figure 1b.

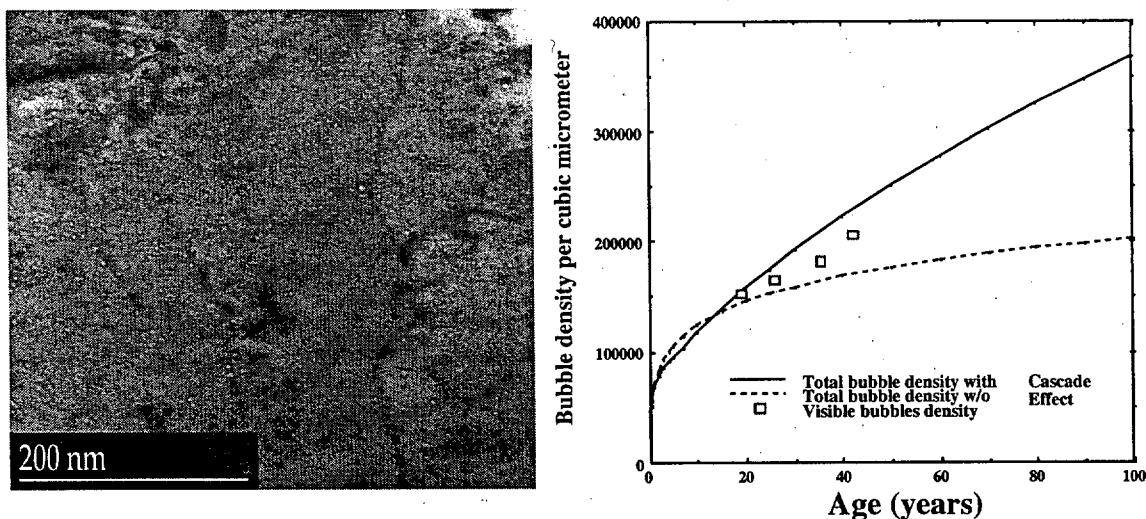


Figure 1. (a) Bright field TEM micrograph of the 42-year old material. The image is taken in the under focus condition such that the bubbles appear as dark rings surrounding bright dots. (b) Model prediction of the bubble number density as a function of age.

The structure and composition of a naturally occurring Pu-Fe intermetallic phase has been determined by combining high energy TEM with simulated and experimental electron diffraction simulation and energy dispersive spectroscopy. A phase belonging to the space group $I4/mcm$ has been identified in a Pu-Ga alloy containing trace amounts of Fe and Ni using electron diffraction and energy-dispersive X-ray spectroscopy (EDXS) in a transmission electron microscope. The plane group symmetry of six experimental diffraction patterns shows that the structure of this phase was at least body-centered orthorhombic. Simulated diffraction patterns, generated from the body-centered tetragonal structure of ζ Pu_6Fe with the space group $I4/mcm$, match the experimental diffraction patterns closely. These results present the first crystallographic evidence for the existence of ζ Pu_6Fe in a Pu-Ga alloy. Figure 2a is a TEM micrograph of the Fe-containing phase in the δ -Pu lattice. Figure 2b is an energy dispersive spectrum showing high levels of Fe. The Pu/Fe ratio of the phase yielded by EDXS was 12.5% and the Pu/(Fe+Ni) ratio was 15.9%. These results suggest that Ni substitutes for Fe in the ζ

Pu_6Fe lattice. By coupling electron diffraction, simulation and EDS, we are able to determine that this is the body centered tetragonal phase $\zeta\text{-Pu}_6\text{Fe}$.

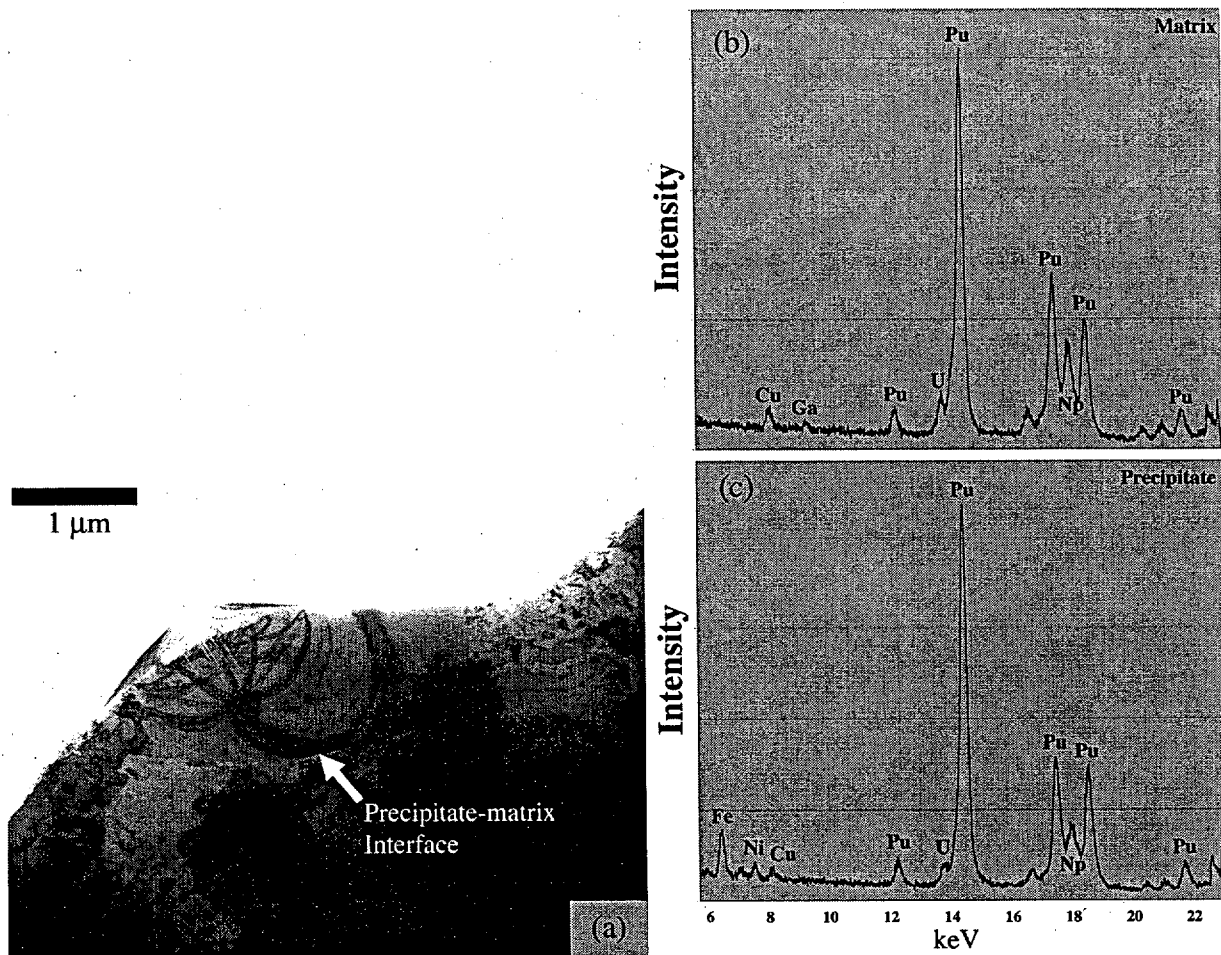


Figure 2. (a) A bright-field TEM image of one of the $\zeta\text{-Pu}_6\text{Fe}$ precipitates contained in a f.c.c. Pu matrix. The precipitate-matrix interface is marked with an arrow, (b) Two EDXS spectra taken from; (a) one of the $\zeta\text{-Pu}_6\text{Fe}$ precipitates and (b) the f.c.c. Pu matrix. Notice that an Fe peak is found in the spectra for $\zeta\text{-Pu}_6\text{Fe}$, but is absent in the spectra for the Pu matrix.

Using high energy-electron energy loss spectroscopy (HE-EELS), TEM, and synchrotron-radiation-based X-ray absorption spectroscopy (XAS), we are evaluating the bonding of the 5f states of Pu. The advantage of this approach is that the HE-EELS experiments are performed in a TEM and are coupled with imaging and diffraction data, therefore, the measurements are completely phase specific. Figure 3a is a TEM image of an α' particle imbedded in a δ -matrix. The microstructure has been produced by cooling the Pu-Ga alloy to 150K for 10 hours. Figure

3d is an electron energy loss spectrum taken from an α' particle embedded in δ -matrix. Implications of these results to our understanding of bonding will be discussed.

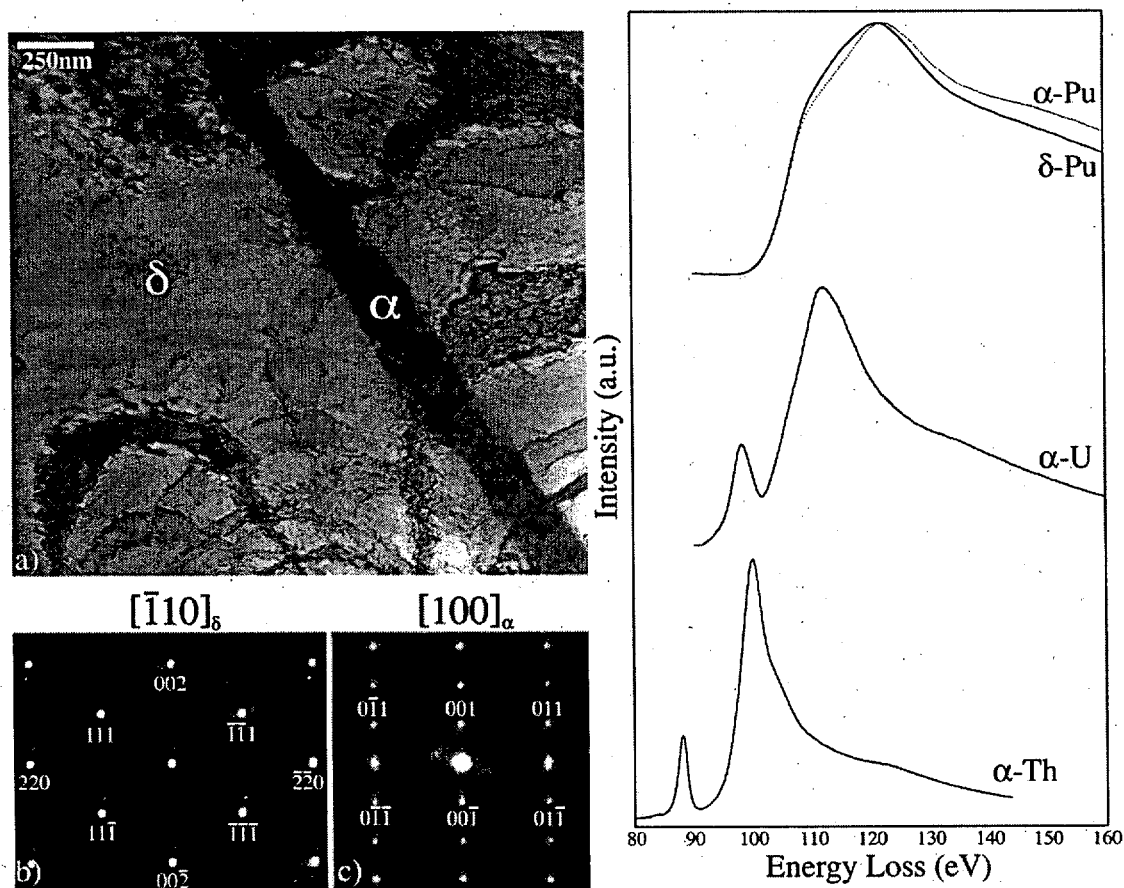


Figure 3. (a) A bright-field TEM image acquired near a $[\bar{1}10]_{\delta} \parallel [100]_{\alpha}$ zone axis showing an α plate in a δ matrix. (b) A $[\bar{1}10]$ diffraction pattern from δ and (c) a $[100]$ diffraction pattern from α , each with a number of reflections indexed, (d) the $O_{4,5}$ ($5d \rightarrow 5f$) absorption edges from α -Th, α -U, α -Pu and δ -Pu acquired by HE-EELS in a TEM. These spectra were collected at an accelerating voltage of 297 keV with an energy resolution of 0.8 eV.

References

1. Howell, R.H., Sterne, P.A., Hartley, J., Cawan, T.E., *Applied Surface Science* **149** (1999) 103-105.
2. Hecker, S.S. and Timofeeva, L.F., *Los Alamos Science* **26** (2000) 244.

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